



# PATENT SPECIFICATION

DRAWINGS ATTACHED

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## COMPLETE SPECIFICATION

### Improvements in Process for Producing Improved Alloys

We, HANDY & HARMAN, a corporation organized and existing under the laws of the State of New York, United States of America, of 82 Fulton Street, New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to internally oxidation-hardened alloys, and has for its object the provision of an improved process for producing non-brittle oxidation-hardened alloys. Another objective is to produce such alloys in larger sections than has heretofore been practical. The process comprises the oxidation of a powdered alloy consisting of a solvent metal and a very small amount of an oxidizable solute metal under controlled conditions to oxidize preferentially the solute metal, and the coalescing and plastic deformation of the oxidized powder to the extent of at least 50% reduction in cross-sectional area. The alloys may be produced in any desired size, not being limited to the small dimensions heretofore necessary, and they do not suffer the intergranular brittleness characteristic of such alloys as heretofore produced.

It is known that metal oxides of fine particle size may be physically mixed with metal powders and the mixture extruded and sintered to coalesce the particles into a continuous piece of metal having increased hardness, strength, and creep resistance, but the gain in strength thus obtained is rather small.

There are also known solid solution alloys, which consist of a non-oxidizable solvent metal capable of diffusing oxygen and a solute metal which forms stable oxides. Such alloys in the form of thin sheets or wires are hardened by heating in an environment that is oxidizing to the solute metals but non-oxidizing to the solvent metals. Hardening is thus obtained by internal oxidation, i.e., by the precipitation of very small refractory oxide

particles in the matrix of the solvent metal. Examples of such alloys are: 99.7% Ag with 0.3% Mg; and 99.75% Cu with 0.25% Al or 0.25% Be. The increase in strength that may be obtained by internal oxidation of such alloys is considerably greater than can be obtained by the simple admixture of oxide powder with metal powder. However, the internally oxidized metal has intergranular brittleness, due presumably to a relatively high concentration of oxide in the grain boundaries of the alloy. Another disadvantage of the internally oxidized alloys is that their use is confined to relatively light sections of strip and wire because the time required for oxidation increases as the square of the diameter or thickness.

We have found that if a powdered alloy susceptible of internal oxidation hardening is first produced, the powder particles can be hardened in a very short time by virtue of their small size and large surface-to-mass ratio. The hardened powders will still have the inherent intergranular brittleness since most individual particles will be polycrystalline. The hardened particles may then be pressed and sintered, or hot pressed, into a billet which may then be cold rolled or, preferably, hot extruded to coalesce the particles into a continuous piece of relatively large cross section, and, if the plastic deformation thus accomplished is equivalent to 50% or preferably 75% reduction in cross-sectional area or more, the benefits shown for strip and wire will then be apparent in pieces of large cross-section, and without the objectionable brittleness.

The process of our invention thus overcomes brittleness, a basic defect in internally oxidized polycrystalline alloys, and provides an alloy which is non-brittle having improved strength, and without size limitations.

In accordance with our invention we form a solid solution alloy of a solvent metal of the group consisting of silver, nickel, copper, and palladium, and solute metals of the group con-

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5 sisting of aluminium, beryllium, and mag-  
 10 nesium in an amount varying from 0.1% to  
 15 5% by weight and reduce this alloy in any  
 suitable way to a powder as by atomizing the  
 molten alloy or by grinding the solid alloy.  
 The powdered alloy is heated in the presence  
 of an oxygen-containing gas such as air under  
 controlled conditions of temperature to oxi-  
 dize only the solute metal. The oxidized  
 powder is compacted and sintered or coalesced  
 into a coherent mass of any desired size or  
 shape at an elevated temperature, and then is  
 subjected to plastic deformation by mechanical  
 working to the extent of at least 50%  
 reduction in cross-sectional area.

20 In carrying out the process of the inven-  
 tion, an alloy was formed of 99.7% of silver  
 as the solvent metal and 0.3% of magnesium  
 as the solute metal. This alloy was melted  
 and was atomized by a blast of air to form a  
 fine powder having an average particle size of  
 40 microns, more or less. The powder was

spread over a tray and heated to a tempera-  
 ture of 1350° F. for 16 hours in the air. Much  
 shorter times may be used if the powder is  
 stirred so as to expose all surfaces directly to  
 the air. For the silver alloys a range of tem-  
 perature of from 1200° F. to 1500° F. may  
 be used. The powder was washed in a dilute  
 solution of hydrochloric acid to remove sur-  
 face oxide film that may have resulted during  
 atomizing. This dissolving of oxide film is  
 unnecessary in practical operations and was  
 used in this case merely for test purposes to  
 eliminate a possible variable. The oxidized  
 powder was much harder than the unoxidized  
 powder as shown by its low compressibility.

The hardened silver alloy powder was  
 pressed in air at 1200° F. to 1500° F. and  
 120,000 psi to produce a flat tablet about  
 0.135 inch thick. This tablet was cold rolled  
 to a thickness of 0.071 inch, annealed at  
 1000° F. and cold rolled to 0.030 inch. The  
 physical properties are listed in Table I:

TABLE I

	Rockwell Hardness	Yield Strength	Ultimate Strength
		psi	psi
45 As pressed	B85	—	—
As rolled 0.071"	B85	—	84,000
Annealed 1000° F.	B85	—	—
As rolled 0.030"	B85	64,600	67,200

50 In order to demonstrate the relative brittle-  
 ness of this alloy, the following procedure  
 was used. In the accompanying drawings,  
 Figure 1 is an edge view of an alloy strip  
 resulting from the above operation; Figure 2  
 is an edge view of a metal frame holding the  
 alloy strip of Figure 1 in curved position, and  
 Figure 3 is a view similar to Figure 2, show-  
 ing the failure of the alloy strip.

55 In carrying out the test, the flat alloy strip  
 or sheet 1, say about 4" long and 1/2" wide  
 and 0.020" thick, is bent into a bow shape so  
 as to produce stress near the yield point in  
 the outer fibers of the strip and placed into  
 60 the rigid frame 2 which holds the strip in this  
 bent shape as shown in Figure 2. Several of  
 these identical assemblies of the bowed strip,  
 each restrained at its ends, were held at room  
 temperature for 20 hours. Those surviv-  
 65 ing were heated at 500° F. for 6 hrs., and

then at 1000° F. for 6 hrs. In this test, the  
 alloys produced by the practices used hereto-  
 fore will crack due to brittleness as shown in  
 Figure 3. Conventional internally oxidized  
 strip will often fail at room temperature, and  
 almost invariably at 600° F or 1000° F. The  
 alloy of this invention does not fail in this  
 test. This elastic bending of the flat piece of  
 metal and holding its ends places the metal  
 under tensile stress near its elastic limit and  
 is a severe test of brittleness.

An extrusion billet 3 1/2" diam. x 4"  
 long was formed from oxidized alloy powder  
 consisting of 99.7% silver and 0.3% mag-  
 nesium according to the invention as above  
 described. The billet was hot extruded at  
 1500° F. from 3.5" in diameter to 0.625" in  
 diameter. The properties of the extruded  
 alloy are listed in Table II.

TABLE II

	Rockwell Hardness	Yield Strength	Ultimate Strength
As extruded	B72	psi 58,800	psi 63,000
Annealed 1000° F.	B71	56,000	63,000
Annealed 1400° F.	B62	56,100	59,000
Annealed 1600° F.	B56	48,800	51,900

5 In a comparative test, silver powder of 1 to 5 micron particle size was mixed with 5% of fine MgO precipitate and extruded at 1500° F. The ultimate strength was only 22,000 psi.

10 Results similar to those listed in Tables I and II can be obtained with copper base alloy powders containing 0.30% beryllium or 0.35% aluminum. In oxidizing the copper alloy powders, one must avoid complete oxidation of the copper as would occur in air. The powder may be heated in air to form an oxide film containing enough oxygen to satisfy 15 the demand of the beryllium or aluminum, and then in the absence of air to permit the diffusion of oxygen into the interior of each copper alloy particle. Oxidizing and diffusing temperatures in the range of 1300° F. to 20 1800° F. may be used. The plastic deformation should be carried out in this same range. The plastic deformation may be done by hot pressing or hot extrusion, preferably at 1600° F.

25 Nickel alloy powder containing from 2% to 5% of aluminum may be treated in a manner similar to that just described for the copper alloy powder but with oxidizing temperatures in the range of 1600° F. to 2200° F.

30 In the prior art of producing internally oxidized alloys, it has been the practice to form thin sheets or wires of the alloy and subject them to oxidation at an elevated temperature. Because the rate of penetration of the oxygen is so slow and the time required 35 for complete penetrating increases as the square of the thickness only thin sheets or wires of prior art alloy can be used in practical operations. With Ag 0.3% Mg alloy, 40 for example, sheets of the thicknesses of 0.015", 0.030", 0.060", and 0.120" must be heated for 1 hr., 4 hrs., 16 hrs., and 64 hrs., respectively at 1350° F. in air to achieve effective oxidation, i.e. for the oxidation to 45 progress through the entire thickness of the sheet, and the product is brittle in the test shown herein. In comparison, the time required for carrying out the oxidation step of the invention does not vary with the mass,

and the resulting product is not brittle.

50 Metal alloy systems other than Ag, Cu, Ni, or Pd solvents with Be, Mg, Al solutes may be processed in accordance with this invention. Any solvent-solute combination that fulfills the following requirements will suffice. 55

1) The solvent must be a ductile metal capable of diffusing oxygen at elevated temperatures below its melting point.

2) The solute metal must have a heat of oxide formation substantially higher than that of the solvent metal. 60

3) The solute metal must be in solid solution at the temperature at which oxidation is to take place.

#### WHAT WE CLAIM IS:—

65 1. The process for producing non-brittle internally oxidation-hardened alloys which comprises making a solid solution alloy consisting of a solvent metal of the group: silver, copper, nickel, and palladium, and from 70 0.1% to 5% by weight of an oxidizable metal of the group: aluminium, beryllium and magnesium, dissolved therein, powdering the alloy, heating the alloy powder in an oxygen-containing gas to oxidize only the dissolved metal without substantially oxidizing 75 the solvent metal to harden said alloy powder, said heating being for a length of time sufficient to oxidize substantially all of the dissolved metal within the alloy powder, to 80 thereby impart internal oxidation hardening to the powder particles, and coalescing the internally oxidized powder into a solid piece by heat, pressure, and plastic deformation to the extent of at least 50% reduction in cross-sectional area. 85

2. In the process of claim 1, plastically deforming the alloy in a hot extrusion operation to the extent of at least 50% reduction in cross-sectional area. 90

3. In the process of claim 1, forming an alloy of silver and a solute metal of the group consisting of magnesium, aluminium, and beryllium.

4. In the process of claim 1, forming an alloy consisting of 99.7% silver and 0.3% of 95 magnesium, heating the powder to a tem-

perature of from 1200° F. to 1500° F. to oxidize the magnesium, coalescing the powder under a high pressure and at an elevated temperature of from 1200° F. to 1500° F. and plastically deforming the alloy to the extent of at least 50% reduction in cross-sectional area.

5. In the process of claim 1, forming an alloy of the group consisting of copper as the solvent metal and a metal dissolved therein of the group consisting of beryllium and aluminum, oxidizing the alloy powder at a temperature of from 1300° F. to 1800° F. under limited conditions of oxidation, then continuing the heating of the oxidized alloy out of contact with gaseous oxygen, and coalescing the oxidized powder and plastically deforming it.

6. The process of producing a non-brittle internally oxidation-hardened alloy which comprises subjecting to controlled oxidation at an elevated temperature an alloy powder consisting of a solvent metal, which does not oxidize substantially under the controlled conditions of oxidation, of the group consisting of silver, copper, nickel, and palladium, and an oxidizable solute metal of the group: aluminium, beryllium and magnesium, in solid solution therein in an amount of from 0.1% to 5% by weight, maintaining the alloy powder under such controlled oxidation conditions for a length of time sufficient to oxidize substantially all of the solute metal within the alloy powder, to thereby impart internal oxidation

hardening to the powder particles, coalescing the powder into a solid piece at an elevated temperature, and plastically deforming the solid piece under mechanical working to the extent of at least 50% reduction in cross-sectional area.

7. In the process of claim 6, plastically deforming the coalesced alloy by rolling.

8. The process for producing non-brittle oxidation-hardened alloys which comprises making a solid solution alloy consisting of a solvent metal capable in the solid state of diffusing oxygen at elevated temperature and from 0.1% to 5% by weight of a solute metal having a heat of formation of its oxide substantially higher than the heat of formation of the oxide of the solvent metal, powdering the alloy, heating the alloy powder in an oxidizing gas to oxidize preferentially the solute metal without substantially oxidizing the solvent metal, said heating being for a length of time sufficient to oxidize substantially all of the solute metal within the alloy powder, to thereby impart internal oxidation hardening to the powder particles, and coalescing the said internally oxidized powder into a solid piece by heat, pressure, and plastic deformation to the extent of at least 50% reduction in area.

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FIG. 1



FIG. 2

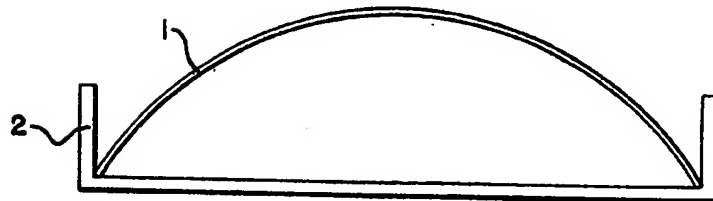


FIG. 3

